Student's document

COLD LIGHT: Investigating analyses using chemiluminescence

Luminescence is light produced without the need for heat, unlike the light from a candle flame or a filament light bulb. It is sometimes called 'cold light'. One form of luminescence is chemiluminescence. It comes from chemical reactions that release energy not in the form of heat (exothermic reactions), but in the form of light energy. Analysis using chemiluminescence is an emerging analytical technique with a range of applications.

Your brief

You are an analytical scientist working in an environmental laboratory. An important part of the laboratory's work is analysis of water, in particular the determination of very low metal ions concentrations in water.

Your manager attended a research seminar recently. She heard about the use of chemiluminescence as an analytical technique. She was particularly interested in one presentation by a university researcher who outlined the potential advantages of chemiluminescence over conventional techniques. He said, "*Chemiluminescence takes its place among other spectroscopic techniques because of its inherent sensitivity and selectivity. It requires no excitation source (as does fluorescence and phosphorescence), only a single light detector such as a photomultiplier tube and no monochromator and often not even a filter. Although not as widely applicable as excitation spectroscopy, the detection limits for chemiluminescent methods can be 10 to 100 times lower than other luminescence techniques.*" The researcher outlined a simple system that used a substance called luminol. Amongst its analytical applications was the determination of concentrations of metal ions.

Your manager has asked the analytical team to find out more about chemiluminescence and its potential use in analysis. She wants you to do some initial research, write a brief report on it and propose a costed research programme to investigate more fully the potential of luminol chemiluminescence in metal ions analysis.

You need to show that, working in a team, you can (a) communicate effectively, (b) manage resources and budgets. How you set about the work depends on the size of the team you have been assigned to for this project.

Your investigation

Plan and prepare

To meet your brief, there are several tasks to carry out. Before starting, each member of the team should read through the tasks and supporting information carefully. Your manager will assign a series of tasks to each team member.

Practical activity

A risk assessment must be carried out before starting practical work.

Task 1: Changes that produce 'cold light' (luminescence)

Carry out some initial investigations into luminescence using these two resources:

- *Inspirational chemistry - resources for modern curricula*: *7.4 Cold light*. Go to http://www.chemsoc.org/networks/learnnet/inspirational/ for instructions. If you are unable to get the instructions, your teacher will provide them.
- **Student sheet***: Oxidation of luminol by sodium chlorate(I)*
  Record all observations and measurements in your laboratory notebook. You may try using a light meter to measure the intensity of the light produced. Also, find out about and explain the difference between fluorescence and chemiluminescence in terms of how cold light is produced.

Task 2: The catalytic oxidation of luminol
The aim of this task is to carry out a series of exploratory investigations into the possible use of chemiluminescence as an analytical technique to determine the concentration of metal ions in solution.

The catalytic oxidation of alkaline solutions of luminol by hydrogen peroxide produces chemiluminescence. A number of metal ions are effective catalysts.

Use **Datasheet***: Oxidation of luminol using hydrogen peroxide* to plan experiments that will enable you to assess the potential of the catalytic oxidation of luminol by hydrogen peroxide for the analysis of metal ions in solution.

You are not likely to obtain quantitative data. However, this is not important. The purpose of the task is to observe whether or not the brightness and duration of any chemiluminescence appears to be affected by the concentration of metal ion catalysts. You need to gather sufficient evidence to propose a more detailed, quantitative study (Task 3).

Work in pairs within your team and assign one of these metal ions to each pair to investigate:
- hexaaquacopper(II), $[Cu(H_2O)_6]^{2+}$
- hexaaquacobalt(II), $[Co(H_2O)_6]^{2+}$
- hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$

You might try using a light meter to compare the intensity of the light produced in different reactions. If so, follow the instructions that come with the meter. It is likely that you will need to work in a darkened room.

Task 3: Proposal for a detailed study
On the basis of the team's investigation, write a costed proposal for a detailed study of the analytical potential of chemiluminescence. Each member should do this for <u>one</u> of the three metal ions that the team investigated.
You need to:
- describe the series of experiments to be carried out, with reasons for the choice
- estimate the cost of the detailed study by considering

\- the price of consumables (chemicals) using chemical suppliers' catalogues
\- approximately how long the experiments will take (take the cost of a chemist's time as £40 per hour, which includes salary and associated costs, building, environmental and other overheads).

Note: If you do not live in the UK, use salaries and overhead costs typical for your own country.

You may find it useful to summarise your plans and data for the costed proposal using **Datasheet***: Data to support costed detailed investigation proposal*

Your findings

Record:

- the results of your initial investigation into cold light and what you found out about the difference between fluorescence and chemiluminescence
- the results of your exploratory investigation into the catalysed oxidation of luminol by hydrogen peroxide.

Write a costed proposal, based on your exploratory investigations, for a more detailed study.

Student self assessment

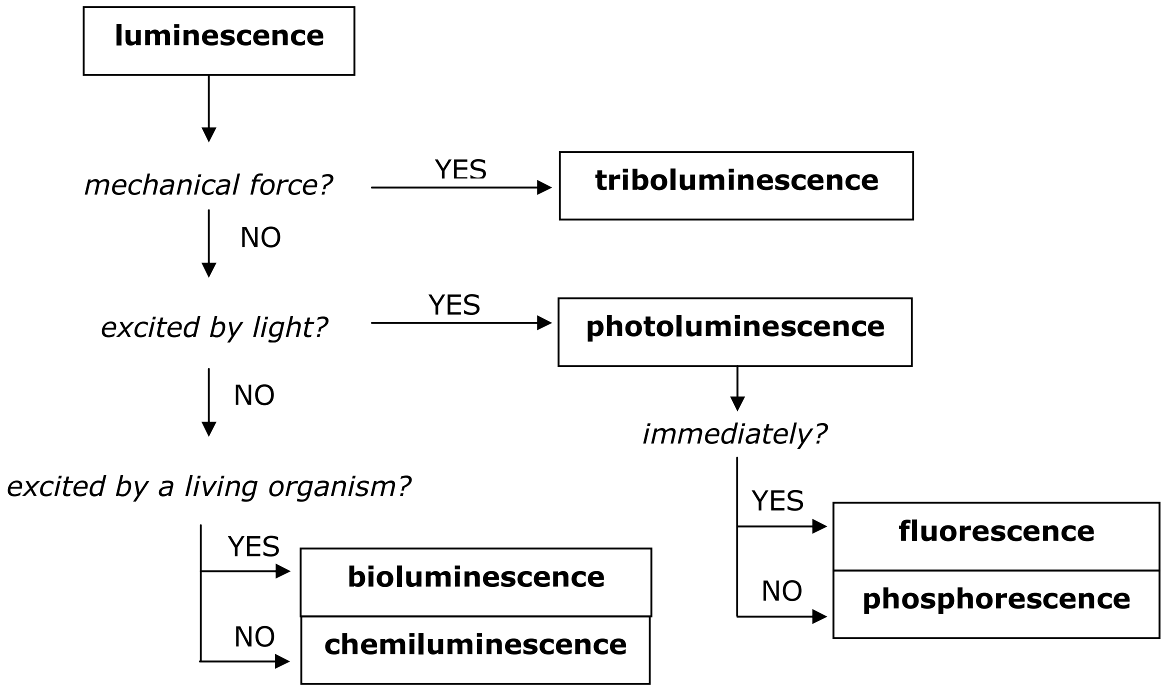
This activity is about using scientific knowledge and understanding to solve problems, working in teams to solve problems, communication and managing resources and budgets. For each case, write about 50-100 words explaining:

- what scientific skills and knowledge you used and how effectively you used them
- how you worked as a pair, giving examples of how you supported one another, and, if appropriate, worked with another pair
- what you learned about managing resources and budgets
- what you learned about communication

Student sheet: Cold light

Based on *Inspirational chemistry- resources for modern curricula*: *7.4 Cold light*.
http://www.chemsoc.org/networks/learnnet/inspirational/

Cold light (luminescence) is light that is emitted when things are cold. There are many types, given different names depending on the conditions under which the light is emitted. The flow chart below shows how you can decide which type of light an object is emitting.



Health and safety

- Do not look at the UV light; always have it pointing away from your eyes and shine it only on the items you are observing.
- Ethanol is flammable – do not use it near flames.
- When using the pliers take care not to crush your fingers.
- Do not eat anything in a laboratory.
- Wear eye protection.

What to do

Set up a table like the one below for your observations.

Item	White light		UV light		Luminescent	Type of luminescence
	on	off	on	off		

1. Cut up the spinach into very small pieces. Wearing eye protection, scrape these into the beaker and just cover them with ethanol. With the beaker on the bench, gently press on the spinach leaves with the glass rod. When the leaves are looking pale and the ethanol is very green, carefully decant the ethanol into the boiling tube and put a bung into it.

2. Using the fluorescent pens, write or colour on the brown paper.

3. In a darkened room, shine a white light on each of the items in turn. Look carefully at the items and note the colour and intensity (bright, dim etc) of any light given off by them. Make sure you observe the spinach extract in the boiling tube from several angles and note any differences.

4. Turn off the light and make the same observations.

5. Repeat the above using UV light.

6. Leave the boiled sweet in its wrapper and place it inside the plastic bag. Make sure that the area where you are working is dark and then crush the sweet using the pliers. Watch the sweet carefully as you crush it.

7. Decide if each item is luminescent and what type of luminescence it shows.

Note for non-UK students
Boiled sweets are hard sweets (made of crystallised sugar). The image below shows an example:

Brown paper is paper that is coloured brown. It is usually used for wrapping parcels. The image below shows an example of a parcel wrapped in brown paper:

Student sheet: Oxidation of luminol by sodium chlorate(I)

This procedure is based on one from the *Practical Chemistry* website: http://www.practicalchemistry.org/experiments/chemiluminescence-cold-light,62,EX.html

Make fresh stock solutions on the day you plan to use them, if they have not already been prepared for you. You will need these solutions:

- Sodium chlorate(I) solution, about 0.08 mol dm^{-3} (solution **A**)
  Add 50 cm^3 of 13% sodium chlorate(I) solution to 950 cm^3 of distilled water in a flask, mix well and stopper.
- Alkaline luminol solution, about 0.002 mol dm^{-3} (solution **B**)
  Put 0.4 g of luminol into a flask containing 4.0 g of sodium hydroxide dissolved in 1 dm^3 of distilled water. Swirl to dissolve the chemicals and then stopper the flask. The luminol does not always appear to dissolve completely, leaving a fine, greenish suspension.

Note: In each case the total volume of each may be scaled up or down.

Procedure

1. Record the temperatures of solution **A** and solution **B**.
2. Lower the room lights and slowly pour 10 cm^3 of each solution simultaneously at the same rate into a boiling tube. Gently shake the tube so that the solutions mix.
3. Record your observations:

- colour/intensity of light produced
- how long it persists
- the temperature of the mixture immediately after mixing and again when the light begins to disappear (it is best to use a fast-response thermometer).

Variations

Plan a series of experiments in which you investigate changing the following:
The concentration of:

- the sodium chlorate(I) solution
- luminol in the alkaline luminol solution
- sodium hydroxide in the alkaline luminol solution.

The temperature of the solutions A and B:

- store solutions in an ice bath and mix them in a boiling tube stood in the ice bath
- store solutions in a water bath at 40 ^oC and mix them in a boiling tube standing in the water bath
- store solutions in a water bath at 60 ^oC and mix them in a boiling tube standing in the water bath

In each case, compare the intensity of the light produced and the time it persists.

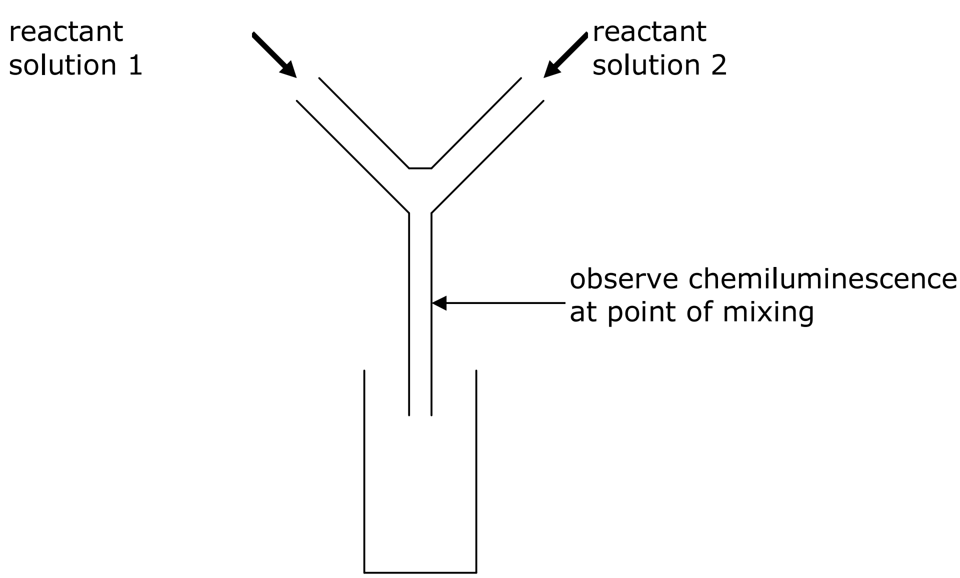
Student datasheet: Oxidation of luminol using hydrogen peroxide

Luminol may be oxidised by hydrogen peroxide in the presence of a suitable catalyst. Catalysts include some metal ions.

The methods given below are based on ones from a number of sources. You may be able to find others.

Notes:

- Some methods may appear very similar. This might suggest to you that they are reliable and worth adapting for your investigation.
- The quantities are those given in the references. Occasionally names and units have been changed according to IUPAC recommendations. To be able to compare methods you may need to convert the units given in one to those used in another.
- You are likely to find that the chemiluminescence is initially very bright, but fades very quickly. This may make it difficult to compare two or more reactions. Consider this idea to make comparisons:
  Slowly pour the two solutions into separate sides of a Y-tube. As they mix, the chemiluminescence is at its brightest. The continuous mixing of reactants will help to prolong this effect.



Catalyst: Cu^{2+}
http://www.shsu.edu/~chm_tgc/JPPdir/JPP1999/

- Luminol solution:

- 1×10^{-3} mol dm^{-3} luminol
- 0.05 mol dm^{-3} sodium carbonate
- 0.3 mol dm^{-3} sodium hydrogencarbonate
- 5×10^{-3} mol dm^{-3} ammonium carbonate
- 1.5×10^{-3} mol dm^{-3} Cu(II) (added as sulfate salt)

- Hydrogen peroxide solution: approximately 0.25%

Approximately 15 cm^3 of the luminol solution is measured into a flat-bottom sample tube and the hydrogen peroxide solution is added drop by drop.

http://qsad.bu.edu/curriculum/labs/Luminol3_1.html

- Luminol solution:

Pour 50 cm^3 of distilled water into a 1 dm^3 conical flask. Carefully add:
- 4.0 g sodium carbonate
- 0.2 g luminol
- 24.0 g sodium hydrogencarbonate
- 0.5 g ammonium carbonate monohydrate
- 0.4 g copper(II) sulfate-5-water

Mix to dissolve the solids (using a magnetic stirrer will help the luminol to dissolve completely). Fill the flask to 1 dm^3 with distilled water and mix. The final solution should have a pH of 9. Test the solution with pH paper, and if its pH is below 9, add a small amount of ammonium carbonate monohydrate to increase the pH.

- Hydrogen peroxide solution:

Pour 50 cm^3 of 3% hydrogen peroxide to a 1 dm^3 conical flask. Fill to 1 dm^3 with distilled water and mix. Final solution is approximately 0.15%.

Use a glass spiral assembly. Place a funnel at the top of the spiral. Place a 2 dm^3 flask under the spiral to collect the solution. Pour about 100 cm^3 of water through the spiral assembly to gauge the flow rate. Discard the water collected in the flask. Dim the lights. Simultaneously pour the luminol and hydrogen peroxide solutions into the funnel. A blue glow can be observed for approximately two minutes after initial mixing.

http://www.glowspace.com/classroom.htm

- Luminol solution:
- 4 g sodium carbonate
- 0.2 g luminol
- 24.0 g sodium hydrogencarbonate
- 0.5 g ammonium carbonate
- 0.4 g copper(II) sulfate-5-water
- 1 dm^3 distilled water

Mix to dissolve.

- Hydrogen peroxide solution:

Dilute 50 cm^3 of 3% hydrogen peroxide to 1 dm^3. Final solution is approximately 0.15%.

Mix about 200 cm^3 of each of the two solutions in a conical flask.

http://www.chm.bris.ac.uk/webprojects2002/fleming/experimental.htm

- Luminol solution:
- 4 g Na_2CO_3
- 0.2 g luminol
- 24 g $NaHCO_3$
- 0.5 g $(NH_4)_2CO_3.H_2O$
- 0.4 g $CuSO_4.5H_2O$

All dissolved in 1 dm^3 H_2O

Mix to dissolve.

- Hydrogen peroxide solution:

50 cm^3 of 30% H_2O_2 diluted to 1 dm^3 in H_2O. Final solution is approximately 1.5%.

Add the hydrogen peroxide solution to the luminol solution. A very bright, fast reaction is observed.

Catalyst: $[Fe(CN)_6]^{3+}$

http://www.york.ac.uk/org/seg/salters/chemistry/ResourceSheets/luminol.PDF
- Dissolve 0.1 g of luminol in 20 cm^3 of sodium hydroxide solution (0.5 mol dm^{-3}) and make up to 100 cm^3 with water.
- Make 100 cm^3 of a 5% solution of potassium hexacyanoferrate(III).

Add small portions of each solution to a beaker and observe the light emitted. You will probably need to darken the room or build an enclosed darkened area. You will also need to measure the amount of light emitted with a light meter. ProBase note: This appears incomplete since the quantity of hydrogen peroxide used is not given.

http://www.chm.bris.ac.uk/webprojects2002/fleming/experimental.htm
Dissolve 4 g Na_2CO_3 in 500 cm^3 H_2O. Add 0.2 g luminol and dissolve. Add 25 g sodium hydrogencarbonate and 0.2 g ammonium carbonate monohydrate. Dilute to 1 dm^3 and use a 25 cm^3 portion for each reaction.

Dissolve 0.76 g $K_3[Fe(CN)_6]$ dissolved in 25 cm^3 of 5% H_2O_2 solution.

Mixing the two solutions gave a lasting glow of more than 50 seconds. Because the catalyst in this reaction is strongly coloured the light appears green.

Catalyst: Co^{2+}

Automated Flow-Injection Instrument for Chemiluminescence Detection Using a Low-Cost Photodiode Detector. A. Economou, D. Papargyris, and J. Stratis, Journal of Chemical Education 2004, 81, 496
Luminol, hydrogen peroxide, sodium hydroxide, and cobalt(II) sulfate-7-water are analytical grade. Distilled water is used to prepare all solutions. Stock solutions required:
- 0.01 mol dm^{-3} luminol
- 10 g dm^{-3} cobalt(II) sulfate-7-water
- 1 mol dm^{-3} sodium hydroxide
- 0.1 mol dm^{-3} hydrogen peroxide (about 0.34%)

Typical starting concentrations:
- luminol: 0.001 to 0.01 mol dm^{-3}
- hydrogen peroxide: 0.002 to 0.02 mol dm^{-3}
- sodium hydroxide: 0.0001 to 0.001 mol dm^{-3}

A calibration graph is constructed using Co(II) solutions in the concentration range 0.5–200 mg/dm^3. A Co(II) solution of unknown concentration is analysed from the intensity of emitted light using the calibration graph.

http://www.chm.bris.ac.uk/webprojects2002/fleming/experimental.htm

- Dissolve 11 g Na_2CO_3, 8 g $NaHCO_3$ and 0.2 g luminol in 1 dm^3 distilled water. Add 25 cm^3 of 3% H_2O_2 solution.
- Dissolve 0.1 g cobalt(II) nitrite in 1 dm^3 H_2O

Mix the two solutions. Less bright than the copper(II)-catalysed reaction, but lasts longer and is useful experimentally.

ProBase note: 'Cobalt(II) nitrite' is almost certainly a mistake in the original text and it should be cobalt(II) nitrate-6-water.

Thinking about the proposal for a detailed study

Here are some ideas you might consider when reflecting on your initial investigations and planning a more detailed study:

- Quantitative measurements of chemiluminescence will be required. How might this be done?
- What reaction conditions might be altered?
- How would you produce a calibration graph?
- Find out about constant flow techniques. How can these be used in the analyses (hint: think about the Y-tube suggestion).

You may well come up with other ideas. Discuss these in your group before starting to write your own proposal.

Student datasheet:
Data to support costed detailed investigation proposal

Variables to be studied in more depth
Summary of the planned experiments
Estimated cost of consumables for the planned experiments
Estimated time required and associated staff costs